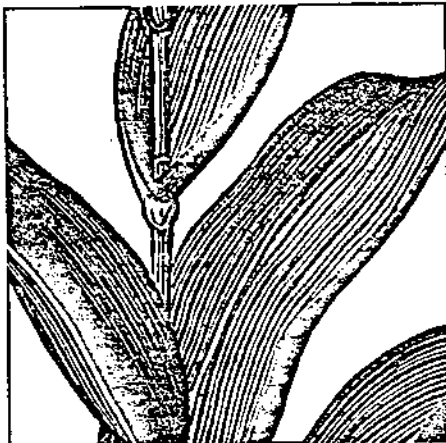


# Selenium responsive diseases in food animals

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## Selenium in Soils and Plants

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### Introduction

Prior to 1960, selenium was important because of its uptake by selenium-accumulator plants and its subsequent toxicity to animals eating these plants. The first reports on the nutritional importance of selenium were published in 1958, and attention was then drawn to another aspect of selenium.<sup>1</sup> The growing incidence of nutritional muscular dystrophy in animals on improved pastures was soon identified as a selenium-responsive disorder (Figure 1). Since then, a large amount of literature has accumulated on various aspects of selenium in the soil-plant animal system. Reviews include those by Alloway et al.,<sup>2</sup> Klayman and Gunther,<sup>3</sup> the NRC,<sup>1,4</sup> and Oldfield.<sup>5</sup> This article reviews the role of soil and plants in selenium cycling to the animal and the return of selenium to the soil.

### Geochemistry

Selenium is widely distributed in trace amounts in nearly all materials of the earth's crust, having an average abundance of about 0.09 ppm.<sup>6</sup> Selenium is only seldom present in concentrations greater than 500 ppm. It is rarely seen in its native state ( $\text{Se}^0$ ) but may be found in association with sulfide ore bodies. During volcanic activity, large quantities of selenium escape as high-temperature volatile gases<sup>7</sup>; thus igneous rocks are usually low in selenium. High concentrations of selenium are found in sedimentary rocks such as shales, with lesser concentrations in sandstones, limestones, and phosphoric rocks.

Nearly 60% of all sedimentary rocks are shales which in turn commonly contain the highest concentrations of selenium. Values range from less than 1 ppm selenium to nearly 300 ppm selenium in the black shales of Permian age from Wyoming.<sup>1</sup> Approximately 2 ppm selenium occurs in the cretaceous pierre shale, which is the parent material for much of the seleniferous soil in the Northern Great Plains of the United States and the Prairie region of Canada. These seleniferous soils may concentrate the selenium to even greater levels upon additional weathering. Shales are also the principal sources of selenium-toxic soil in Ireland, Australia, Israel, and several other countries of the world.<sup>1</sup>

The relatively high concentration of selenium in some phosphate rocks, particularly Western phosphates, is significant because of the wide use of phosphate fertilizers. Robbins and Carter suggested that normal superphosphate can be expected to retain about 60% and concentrated superphosphate about 40% of the selenium in the original rock.<sup>8</sup> The reduction in selenium retention results from volatilization of selenium during the smelting process.

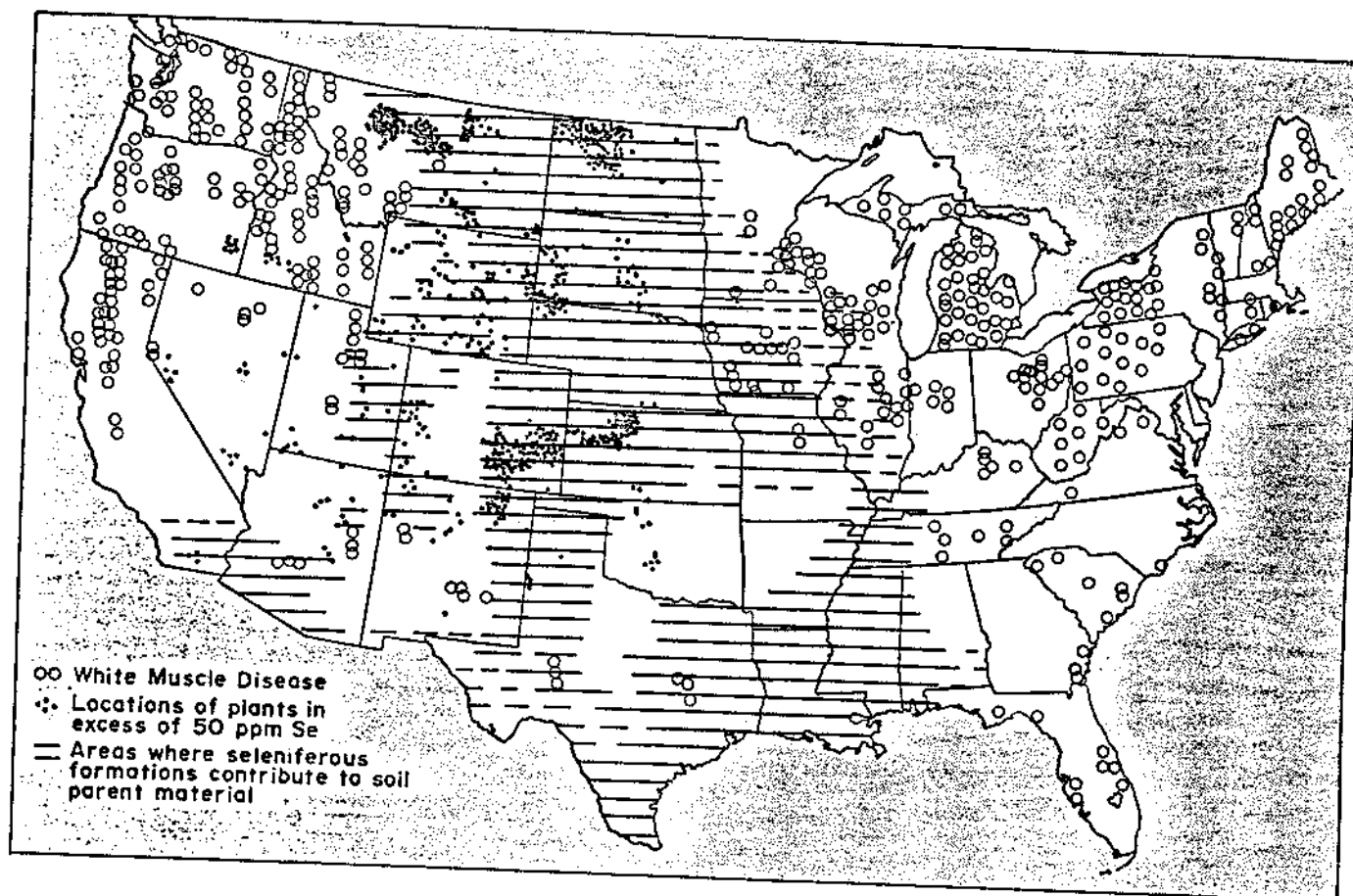
Known deposits of selenium are insufficient to permit mining just for the selenium. Most commercially available selenium is extracted from copper refinery slimes along with the recovery of other precious metals.<sup>1</sup> Total production in the free world was 1.1 million kg in 1973. Selenium is used in the manufacture of glass and electronic equipment and as a

reagent in remedies for eczemas, fungus infections, antidandruff products, veterinary therapeutic agents, injectables, and feed additives.

### Selenium in Soil

The concentration of selenium in most soils lies within the range of 0.1 to 2 ppm; however, high concentrations up to 1200 ppm total and 38 ppm selenium as water-soluble selenate have been reported in seleniferous areas of the world.<sup>6,9</sup> Soils developed from the cretaceous shale of South Dakota, Montana, Wyoming, Nebraska, Kansas, Utah, Colorado, and New Mexico tend to have high selenium values ranging from 2 to 10 ppm.

Low-selenium soils include those derived from sedimentary rocks that predate the major cretaceous period, like those in the northeastern United States.<sup>1</sup> Other low-selenium soils include those in the Pacific Northwest that are formed from recent volcanic ash deposits or loessial material derived from the ash. Soils in the very low-selenium region of the South Atlantic seaboard are formed from well-washed coastal deposits. The soil parent materials of the low-selenium areas in Montana and parts of Idaho are mostly derived from granites and old metamorphic rocks. Low total selenium concentrations occur in the tertiary volcanic rocks of Arizona and New Mexico. Most of the soils from low selenium areas of the United States contain less than 0.5 ppm selenium. Many of these low-selenium areas correspond to areas where



**Figure 1**—The relationship of white muscle disease to the distribution of naturally occurring selenium in the United States.<sup>34</sup>

selenium-responsive disorders, like white muscle disease, can occur (Figure 1). As with other elements, though, the total concentration of selenium in soils shows little relationship to the concentration of selenium in plants grown on those soils.<sup>4</sup> This is because selenium in soil exists in several chemical forms which differ widely in their solubility and availability to plants. These chemical forms are

- Selenides,  $\text{Se}^{2-}$
- Elemental selenium,  $\text{Se}^0$
- Selenites,  $\text{SeO}_3^{2-}$
- Selenates,  $\text{SeO}_4^{2-}$  and
- Organic selenium.<sup>19</sup>

The chemical forms of selenium present in soils and sediments are closely related to the oxidation-reduction potential and pH of the soil. Inorganic selenium exists in the selenate or selenite form in aerated alkaline soils. In

poorly aerated acid soils, inorganic selenium exists as selenide or elemental selenium. The principal chemical reactions of selenium in soils and weathering sediments have been summarized in a schematic drawing by Allaway.<sup>11</sup> This was later modified by Reuter<sup>7</sup> and is shown in Figure 2.

Thus, soils will be low in selenium if formed from parent materials that are low in selenium under acid or alkaline conditions. The greater the amount of rainfall and the more acid the soil, the greater is the likelihood of extremely low-selenium concentrations in the plants.<sup>1</sup> In contrast, aerated, neutral-to-alkaline soils are unlikely to produce selenium-deficient plants.

#### Selenium in Water

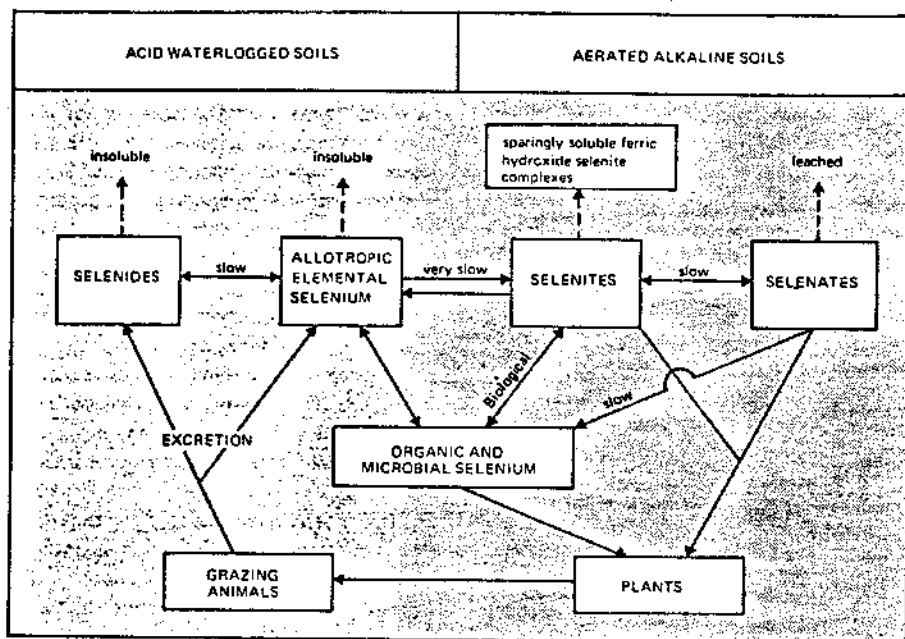
Selenium occurs as a minor constituent in drinking water in a concentration range of 0.1 to 100  $\mu\text{g/L}$ .<sup>2</sup> Samples rarely exceed the 10  $\mu\text{g/L}$  upper limit established by the United States Department of Health Education and Welfare in 1962.<sup>2</sup> Rivers draining some of the seleniferous regions may contain considerably high selenium levels. Irrigation drainage

water from seleniferous soils has contained as much as 2680  $\mu\text{g/L}$ .<sup>1</sup> Very small concentrations of the element are found in lakes possibly because it is precipitated with oxides of such metals as iron and manganese.

Recent studies have reported up to 4200  $\mu\text{g}$  selenium/L in some irrigation drainage water of the productive San Joaquin Valley.<sup>12</sup> The drainage water apparently passes through a seleniferous subsoil strata and picks up soluble selenium forms which are carried into the Kesterson Reservoir near Gustine, California. The high-selenium concentrations are effecting signs of toxicosis in the local wildlife and water fowl.

#### Selenium in Plants

Rosenfeld and Beath<sup>13</sup> and Shrift<sup>14</sup> divided plants into three groups on the basis of their ability to accumulate selenium when grown on high-selenium soils. The first two groups of plants are referred to as *selenium accumulator* or *indicator* plants. These grow well on soil containing high levels of available selenium and have been used to locate seleniferous soils. Plants in Group 1 are called *primary*



**Figure 2**—The postulated cycle of selenium in soil. The broken arrows indicate a process leading to loss of "biologically active" selenium.<sup>7</sup>

indicators and include many species of *Astragalus*, *Machaeranthera*, *Haplopappus*, and *Stanleya*. They normally absorb high concentrations of selenium, often several thousand parts per million.

Plants in Group 2 are referred to as secondary selenium absorbers. They belong to a number of genera, including *Aster*, *Astragalus*, *Atriplex*, *Castilleja*, *Grindelia*, *Gutierrezia*, *Machaeranthera*, and *Mentzelia*. They rarely concentrate more than a few hundred parts per million of selenium. Fortunately, plants in Groups 1 and 2 are not generally grazed under normal conditions.

Plants in Group 3 include grains, grasses, and many forbs that do not accumulate selenium in excess of 50 ppm when grown on seleniferous soil.

Some plants growing on seleniferous soils accumulate surprisingly low levels of selenium. White clover (*Trifolium repens*), buffalo grass (*Hilaria belangeri*), and grama (*Bouteloua* spp.) are poor accumulators of selenium.<sup>1</sup> On the other hand, high-sulfur-containing plants like the Brassicas mustard, cabbage, broccoli, cauliflower, and other Cruciferae are relatively strong concentrators of

selenium. Absorption of selenium and sulfur may be correlated.<sup>14</sup>

Of plants growing on moderately low-selenium soil, alfalfa accumulates more selenium than does red clover (*Trifolium pratense* L.), timothy (*Phleum pratense* L.), or bromegrass (*Bromus inermis* Leyss.). No definite differences have been noted among species growing on very low levels of available selenium. Crops growing on neutral or acid soil absorb very little selenium, and any attempt to increase crop-selenium uptake by shifting to some other species is not likely to be successful.<sup>15</sup> However, Davies and Watkinson reported that a marked difference in selenium concentration between species was apparent under New Zealand conditions of low-selenium soil.<sup>16</sup> The concentration was greatest in a native grass (*Agrostis tenuis* Sibth.) and least in white clover (*Trifolium repens* L.). The selenium values of orchard grass (*Dactylis glomerata* L.) and ryegrass (*Lolium perenne* L.) fell between the extremes.

The selenium in forages and cereal grains may not differ much among species in areas where available selenium levels in the soil are low. Selenium concentrations in legumes and grasses vary when these plants are grown on selenium-normal soils; however, alfalfa usually contains the highest level, and this may be two to ten times as much as is in the grass forage.<sup>17</sup> In areas where soil selenium levels are normal, wheat (*Triticum aestivum*

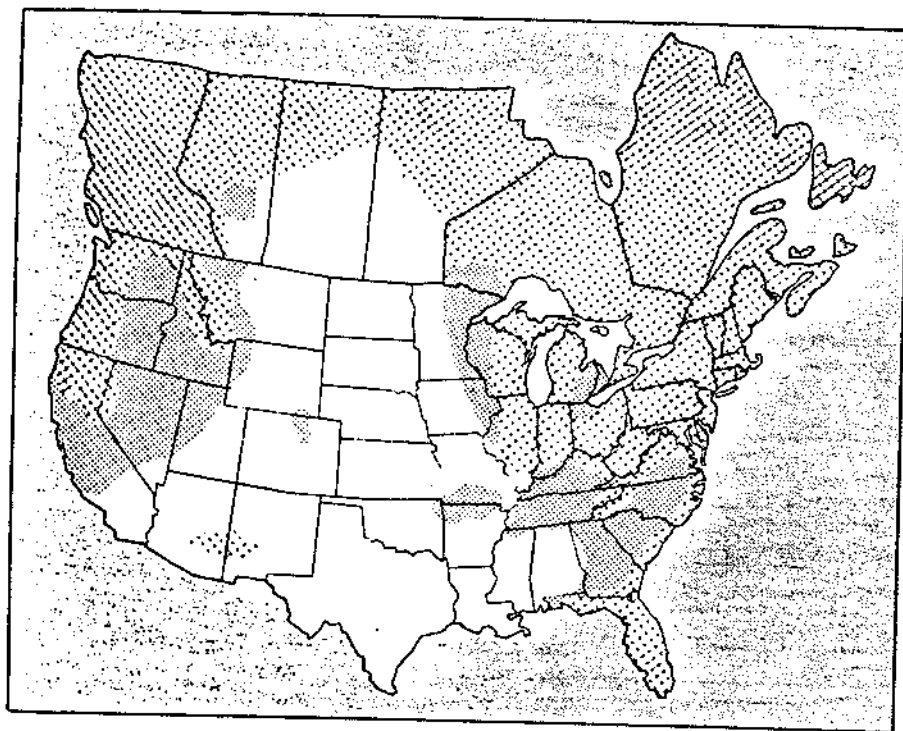
L.) grain has been shown to contain higher selenium concentrations than oats (*Avena sativa* L.) or barley (*Hordeum vulgare* L.).

Selenium is not yet considered an essential element for plant growth. Several early reports indicated that selenium was an essential element for the growth of certain accumulator plants. More recent studies have failed to verify the beneficial effect of selenium in the accumulator plants. Also, a growth depression has been found in alfalfa and subterranean clover (*Trifolium subterraneum*) when they are grown in the presence of 2 ppm selenium as selenite or selenate.<sup>1</sup>

Shrift has summarized the findings on the many chemical compounds of selenium isolated from plants.<sup>14</sup> Much of the selenium in nonaccumulating species is found in the form of protein-bound selenomethionine.<sup>1</sup> In contrast, the selenium in accumulator plants is mostly water soluble and is not associated with the protein. Shrift noted some biochemical distinctions between selenium-accumulator and selenium-nonaccumulator *Astragalus* spp.<sup>14</sup> Selenium-methylselenocysteine was found in much higher amounts in the accumulator than in the nonaccumulator species. Species from both groups methylate selenomethionine to selenium-methyl-selenomethionine, but only the accumulators convert selenomethionine to selenohomocysteine and selenium-methylselenocysteine. Another distinction is the existence of a large amount of selenocystathionine in accumulator species and only trace amounts in nonaccumulator plants.

The selenium metabolites in plants are analogs of sulfur compounds. Nevertheless, selenium metabolism in plants cannot be identified from known mechanisms involving selenium metabolism.<sup>14</sup> Our understanding of the metabolic pathways for selenium in plants remains very limited.

Many microorganisms can reduce selenite to elemental selenium, and some bacteria and fungi have been found that reduce selenite or selenate to volatile, organic selenium compounds.<sup>14</sup> Sulfur-selenium antagonism occurs in the microorganisms. The reduction of selenite is enzymatically mediated. It is now known that many isolated enzyme systems can utilize sulfur and selenium analogs interchangeably. What was traditionally thought to be the mechanism of selenium toxicity, namely, a general interference with the enzymes involving sulfur assimilation, has proved to be more complex.<sup>14</sup>



**Figure 3**—Regional distribution of forages and grain containing low (cross-hatched, 80% less than 0.1 ppm selenium); variable (stippled, 50% greater than 0.1 ppm selenium); or adequate (white, 80% greater than 0.1 ppm selenium) levels of selenium in the United States and Canada.<sup>1</sup>

#### Selenium in Animal Feedstuffs

The selenium content of feedstuffs varies with plant species and geographical area of production (Figure 3). The concentration of selenium in the plant is determined not so much by the amount of total selenium present but by the availability of the element in the soil. In some areas of the United States, forages contain such high levels of selenium that they cause selenosis in livestock (Figure 1). In other areas, the selenium concentrations in crops and forages do not meet animal requirements. There are extensive areas in the country where virtually all the crops and forages contain sufficient selenium to meet livestock requirements.

#### Fate of Fecal, Urinary, and Pulmonary Selenium

Urine is the primary route of selenium excretion by monogastric animals, regardless of whether the selenium is given orally or in-

jected. The main route of selenium excretion in ruminants, though, is a function of the method of administration and the age of the animal.<sup>1</sup> When selenium is ingested by ruminants, most of it is excreted in feces. In contrast, selenium that is injected either intravenously or subcutaneously into ruminants is excreted mostly in urine. Lambs, and presumably calves, that have not developed rumen function can excrete 66 to 75% of the orally ingested selenium in the urine. Thus rumen organisms undoubtedly contribute to this age effect.

Nearly all of the selenium excreted in the feces of ruminants is in insoluble form, and very little is available for uptake by plants. Peterson and Spedding showed that less than 0.3% of the selenium taken up by three pasture plants originated from the selenium contained in sheep manure during a 75-day study.<sup>18</sup> The manure was obtained from sheep dosed orally with isotopic-labeled selenite.

Trimethylselenonium ion ( $\text{TMSe}^+$ ) is an important urinary selenium metabolite. When added to nutrient solutions,  $\text{TMSe}^+$  was readily absorbed and translocated to leaves and stems, but not the grain of wheat.<sup>19</sup> Large differences were observed in selenium uptake by barley, wheat, and alfalfa when  $\text{TMSe}^+$  was applied in a soil-pot study in the

greenhouse. The authors noted that very little of the selenium from  $\text{TMSe}^+$  was absorbed by plants. In addition, some of the  $\text{TMSe}^+$  was lost to the atmosphere through volatilization from the plant. It is likely that the  $\text{TMSe}^+$  excreted in animal urine contributes little biologically active selenium to plants because it is not metabolized. A portion of the  $\text{TMSe}^+$  added to soil was volatilized, and this loss was increased by liming.<sup>20</sup> In addition, 30 to 50% of the  $\text{TMSe}^+$  added to several different soils was fixed during a 21-day period. The biologically inactive  $\text{TMSe}^+$  in urine plus the stimulation of plant growth by the added nitrogen and sulfate in urine may explain the lowered selenium contents in grass at urine patches.<sup>21</sup>

Under certain conditions, significant quantities of selenium are eliminated as a volatile compound having a garliclike odor. This is dimethyl selenide, which is formed by methylating selenite. The amount exhaled increases with increasing selenium intake and is greater for orally administered selenite than selenate, selenomethionine, or seleniferous wheat.<sup>22</sup> The formation of dimethyl selenide can be inhibited by arsenite, cadmium, and other heavy metals. This method of selenium excretion is an important mechanism by which the animal eliminates selenium from the body. The fate of the exhaled dimethyl selenide is unknown.

#### Selenium Pollution

The amount of selenium entering the atmosphere from the burning of fossil fuel is about six times greater than that emitted by mined ores.<sup>23</sup> The fact that selenium deficiencies in livestock occur in the northeastern United States, where fossil fuel consumption is high, indicates that airborne selenium may not be a major factor in environmental concentration of this element.

The application of fly ash to soil, first as a means of disposal, but secondly as a source of some minerals, has been tested.<sup>24,25</sup> Crop yields were generally unaffected, but selenium concentrations were elevated to levels that were adequate for animal nutrition.

Volatile selenium compounds are naturally released as a result of biological activity in soil and water ecosystems. Dimethyl selenide is the principal compound released from soils, lake sediments, and sewage sludge by microbial activity.<sup>26</sup> The same compound is released enzymatically from living plants. A wide variety of fungi, yeasts, and bacteria are

known to methylate selenium into volatile forms, the predominant one being dimethyl selenide, which can now be measured in the atmosphere.<sup>26</sup> Crop plants can absorb dimethyl selenide from the atmosphere and metabolize it, primarily to selenite and selenomethionine. After that it is incorporated into cellular proteins.<sup>26</sup>

### Selenium as a Fertilizer

The clay fraction and organic matter content in soil play a major role in the availability of selenium, especially selenite, which is readily bound.<sup>14</sup> Selenate is less readily bound and is increasingly more soluble in finer-textured soils or soils with higher organic matter concentrations.<sup>14</sup> Selenate is usually absorbed more readily by plants than is selenite. This difference is attributed to the relative ease with which selenite is absorbed to clay or reduced to elemental selenium. There is also a probable difference in permeability at the root membrane. Sulfate, which exerts little effect on selenite uptake, though, influences the absorption of selenate.<sup>27</sup>

The development of safe and effective applications of selenium fertilizer is plagued by a number of problems. First, there are large differences in the solubilities of the various selenium forms. Second, changes may occur in the valence state of soil-applied selenium which in turn affects the solubility with time.<sup>28</sup> Third, there is not much difference between animals' requirement of 0.05 to 0.3 and the toxic level of 2 to 3 ppm selenium. A fourth factor is the physical limitation of uniformly distributing a few grams of a solid fertilizer over a hectare of land.

The application of lime or companion fertilizers containing phosphate, sulfate, or nitrogen can also affect forage selenium concentration in plants.<sup>29</sup> These materials may contain small amounts of selenium, or they may stimulate root growth and subsequent uptake of soil selenium. The author's experience, though, is that the application of these materials often stimulates forage yields, thereby diluting the selenium concentration.

The application of sulfate fertilizers can simultaneously stimulate plant growth and compete with soil selenate for absorption sites on the root and transport mechanisms in the plant. Increasing the concentrations of sulfur in the forage also has detrimental effects on selenium availability to the animal.<sup>30,31</sup> Introduction of irrigation to previously dry-cropped areas is another production practice that usually reduces the selenium content of forages.

There is some risk associated with the application of selenates to acid and neutral soil.<sup>7</sup> Because selenates are more stable in these soils, the uptake of selenium by plants is greater than with selenite applications, and toxicities can occur. Experience has shown that the use of selenate fertilizer results in much higher levels (often toxic to animals) of selenium in the first cut of forages following fertilization. Selenium concentrations in the forage then decrease sharply with each subsequent harvest.<sup>7</sup>

The addition of selenite to acid or neutral soils results in immobilization of some selenium. This process includes sorption of selenite, probably by hydrous sesquioxides, which reduces the solubility of selenium to plants so that they can take up protective but not toxic levels of selenium. The other major process resulting in the immobilization of selenium is the reduction of selenite to  $\text{Se}^0$ , selenide, or both. This reduced selenium apparently is unavailable to plants in the short term, and its oxidation to more available forms may be slow.<sup>32</sup>

The application of 10 g selenium/hectare as selenite to pasture has been suggested.<sup>33</sup> The selenium is applied with a carrier fertilizer such as calcium ammonium phosphate. A method now legally used in New Zealand is the top dressing of pastures with selenium prills.<sup>33</sup>

Caution must be used in fertilizing with selenium to alleviate selenium deficiencies. Inadvertent toxicities can occur because of variations in selenium availability and uptake from different kinds of soil by many different forage species.<sup>5</sup>

### Summary

Reuter summarized the essential features of the selenium cycle in the soil as follows:<sup>7</sup>

1. In acidic, poorly aerated soils, selenium is not available to plants and exists as insoluble selenides and elemental selenium. It is available in aerated acid and neutral pH soils where selenites form and in aerated alkaline soils where selenates are present. In some soils, organic selenium may be oxidized to forms available to plants. Transformations from one oxidation state to another take place slowly.
2. Elemental selenium is stable in soils but can be slowly oxidized by microbiological and chemical processes, particularly at high pH.
3. The rate of reduction of selenite to elemental selenium varies from soil to soil but is apparently independent of pH. This reduction of selenite would have important short-term effects because reoxidation to plant-available forms is appreciably slower than the reduction process.
4. Selenites are strongly sorbed or occluded by reactive iron oxides to form sparingly soluble ferric hydroxide-selenite complexes. These compounds are apparently the predominant form of selenium in most soils low in available selenium.
5. Selenates form somewhat soluble salts with cations present in alkaline soils and can therefore be removed by leaching. They can accumulate in the soil in arid regions. Selenates are not sorbed on reactive iron oxides.
6. Biological processes can convert organic selenium to selenites and vice versa. Selenates are slowly converted to organic selenium.
7. Selenium is inefficiently absorbed from the alimentary tract of ruminants, particularly at low levels of dietary intake. Urinary and fecal selenium are returned to the soil in forms that are unavailable to plants.

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